Opal-CT precipitation in a clayey soil explained by geochemical transport model of dissolved Si (Blégny, Belgium)

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Dissolved Si (DSi) exported by rivers are controlled by geological, hydrological and biological cycle processes [1]. The DSi concentrations measured in a river of an upstream catchment in eastern Belgium (Blégny, Land of Herve) don't vary seasonally (6.91±0.94mgL^{-1}; n=363). Si concentrations in pore water are often higher and vary more (8.65±3.65mgL^{-1}; n=128). The decrease of DSi along the flowpath of water is due to sink processes, i.e. precipitation, adsorption or uptake by vegetation. As the DSi in the river does not show any seasonal variation, uptake by vegetation can be ruled out [1] whereas precipitation or adsorption can control the DSi drained by the stream water. This hypothesis is confirmed by XRD and DeMaster analysis. At 0.1m depth the soil is constituted of 62% quartz, 7% K-feldspar, 6% plagioclase, 3.2% carbonates, 18.9% Al-clay, 1.47% Kaolinite, 0.63% Chlorite and 0.2% amorphous Si, probably of biogenic origin. At 1.5m depth, the amounts of several minerals (35.8% quartz, 0.6% K-feldspars, 0.9% plagioclase, Al-clay 14.7%) drop drastically. Carbonates, chlorite and kaolinite are absent whereas 40.4% opal-CT appears. The precipitation of opal-CT controls the DSi export of this catchment.

To describe DSi export from a catchment a geochemical transport model is developed in HP1 which couples the water flux model Hydrus with the geochemical model PHREEQC [2]. Our model is based on the conceptual model developed in [3]. First results show different DSi export dynamics in the unsaturated zone than in the aquifer due to different pCO_2 values and varying soil moisture conditions. Further development of the model will help to find out the reason of opal-CT precipitation in this setting.

[1]Fulweiler, Nixon (2005) *Biogeochemistry* **74**:115–130. [2] Simunek, Jacques, van Genuchten, Mallants (2006) *JAWRA* **42**:1537-1547. [3] Ronchi *et al*. (2013). *Silicon*, **5(1)**, 115–133.

Constraining the origin of sulfur isotopic variability through the end-Ordovician Hirnantian glaciation and mass extinction

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Geochemical records of the end-Ordovician Hirnantian Stage show parallel positive excursions in the stable isotope compositions of sedimentary pyrite sulfur ($\delta^{34}S_{pyr}$), organic carbon, and carbonate carbon; these isotope excursions coincide with the end-Ordovician glaciation and mass extinction. An increase in pyrite burial attributed to marine anoxia has been proposed to explain the sulfur isotope excursion and link oceanic redox conditions to the extinction of marine fauna. Such an increase in pyrite burial would generate a parallel excursion of equal magnitude in the isotopic composition of coeval marine sulfate. However, paired sulfur isotope data from the Hirnantian Stage of Anticosti Island, Quebec, do not covary, which suggests enhanced pyrite burial is not the cause of the Hirnantian $\delta^{34}S_{pyr}$ excursion and questions the role of anoxia in the mass extinction. We present new high-resolution paired sulfur isotope data from carbonate-associated sulfate (CAS) and pyrite during the Hirnantian Stage from the Girardeau Formation, Missouri, USA, to test these hypotheses. The results show a 28‰ enrichment in $\delta^{34}S_{pyr}$ but no parallel excursion in $\delta^{34}S_{CAS}$, indicating that enhanced pyrite burial did not generate the Hirnantian $\delta^{34}S_{pyr}$ excursion. These observations may best be explained by a transient reduction in the expressed isotopic fractionation during microbial sulfate reduction associated with Hirnantian sulfur cycling possibly caused by: a change in actual biological fractionation; a shift in the chemocline leading to restricted exchange of porewater sulfate; or glacio-eustatic sea-level drawdown corresponding to syndepositional sediment reworking and increased oxidation.

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